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Analytical methods for determining nitroguanidine in soil and water

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Methods were developed for determining nitroguanidine in soil and water. The soil method involves extracting a 2-g sample with water using an ultrasonic bath. Soil extracts and water samples are filtered through a 45-μm membrane prior to determination by RP-HPLC. Separations are achieved on a mixed-mode RP18/cation column eluted with 1.5 mL/min of water; detection is by UV (λ = 263 nm). Certified reporting limits were estimated at 5.0 μg/L for water and 0.5 μg/L for soil.

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PREFACE

This report was prepared by Marianne E. Walsh, Research Physical Scientist, Applied Research Branch, Experimental Engineering Division, U.S. Army Cold Regions Research and Engineering Laboratory. Funding for this research was provided by the U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, Maryland (R-90 Multi-Analytical Services), Martin H. Stutz, Project Monitor.

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MARIANNE E. WALSH

INTRODUCTION

For many years the making of munitions for the Army resulted in contamination of the environment surrounding production sites. In the 1970s, the Army sought to correct this situation by identifying and cleaning up affected areas. As part of this effort, the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), under the Installation Restoration Program, has been actively developing analytical methods for detecting unique military compounds, such as explosives and propellants, in environmental samples. Under the auspices of USA THAMA, the U.S. Army Cold Regions Research and Engineering Laboratory has been charged with developing methods for nitramines, nitroaromatics, tetrazene, and, most recently, nitroguanidine in water and soil.

Nitroguanidine ($HN = C(NH_2)NHNO_2$) is a component, along with nitroglycerine and nitrocellulose, of triple base propellant. Its relatively high solubility in water (4.4 g/L) (U.S. Army 1984) increases the likelihood of groundwater contamination when water used to clean cutting blades and wash-out buildings is disposed.

Table 1. Physical properties of nitroguanidine (U.S. Army 1984).

Empirical formula	$CH_4N_4O_2$
Molecular weight	104
Crystal density (g/cm³)	1.72
Melting point (°C) (decomposes)	232
Solubility (g/L)	
water 25°C	4.4
water 100°C	82.5
CAS reg no.	[556-88-7]

CHEMISTRY

The physical properties of nitroguanidine (NQ) are listed in Table 1. As a pure substance, nitroguanidine exists in two crystal forms, alpha and beta, which have the same melting point (U.S. Army 1984). The alpha form, whose crystals develop into long, thin, flat needles, is most commonly used as an explosive. The two forms differ slightly in water solubility, but their solubility curves cross at 25 and 100°C and have values of 4.4 and 82.5 g/L at these two temperatures (U.S. Army 1984). Thus, nitroguanidine has a water solubility an order of magnitude greater than most other explosives, such as TNT and RDX. NQ is sparingly soluble in ethanol, methanol and acetone. It is essentially nonvolatile.

Nitroguanidine in aqueous solutions exists in the two tautomeric forms shown in Figure 1 (Kemula et al. 1970, Kaplan et al. 1982). The nitroimine exists in acidic, neutral or slightly basic solutions.

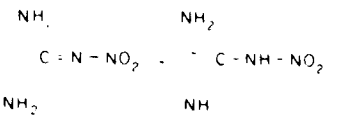

Figure 1. Chemical structure of nitroguanidine.

ANALYTICAL METHODS

Nitroguanidine's physical and chemical characteristics preclude analysis by gas chromatography, but several liquid chromatographic methods (Table 2) have been developed using both UV and electrochemical detection. Most of these methods use a reversed-phase C8 or C18 column (Kaplan et al. 1982, Burrows et al. 1984, Maskarinec et al. 1986, Ogle and Westerdahl 1986, Manning and Maskarinec 1987) eluted with a mobile phase that is pre-

Table 2. Summary of high-performance liquid chromatographic methods for nitroguanidine.

Column	Mobile phase	Retention time (min)	Concentration range	Reference
Dupont Zorbax ODS (25 cm × 4.6 mm)	90/10 water–methanol	2.8	100 µg/L (water) 1 µg/g (soil)	Kaplan et al. (1982)
Dupont Zorbax C8 (25 cm × 4.6 mm)	water 0.8 mL/min	6.0	0.5–10 mg/L	Burrows et al. (1984)
Dupont Zorbax C18 (25 cm × 4.6 mm)	20/80 propanol-aqueous sodium acetate	5.0	—	Maskarinec et al. (1986) Manning and Maskarinec (1987)
C8	water 3 mL/min	1.78	0.5–26 mg/L	Ogle and Westerdahl (1986)

dominantly water. Nitroguanidine is not well retained on these columns and elutes early, making interferences likely when environmental samples are analyzed. This report outlines the development of a High Performance Liquid Chromatographic (HPLC) method for the analysis of nitroguanidine in soil and water samples. Separation is achieved using a mixed mode RP18/cation exchange column.

EXPERIMENTAL METHODS

Instrumentation

The RP-HPLC determinations were made using two systems. One system was composed of a Perkin Elmer Series 3 pump and a Perkin Elmer LC-65T variable wavelength UV detector. The other system was composed of a Spectra Physics SP8810 pump and a Spectra Physics SP8490 variable wavelength UV detector. Both systems were interfaced with a Dynatech Precision Sampler Model LC-241 autosampler containing a Rheodyne Model 7010A sample loop injector with a 100-µL sampling loop. Data were recorded on a Hewlett Packard 3393A digital integrator set in peak height mode and saved using a Hewlett Packard 9114B disk drive. Data were also recorded on a Linear Model 500 strip chart recorder.

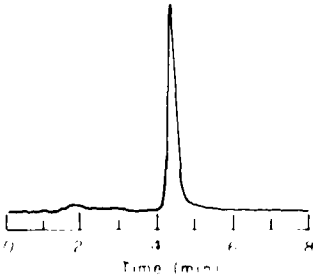

Figure 2. Chromatogram of aqueous nitroguanidine (190 µg/L) on a RP18/cation exchange column eluted with 1.5 mL/min of water.

Separations were achieved on a mixed mode RP18/cation exchange column (Alltech Associates) that was eluted with 1.5 mL/min of degassed water. Retention time for nitroguanidine was 4.4 minutes. Figure 2 shows a typical chromatogram.

Chemicals

Nitroguanidine was obtained from Aldrich and was recrystallized from water. The crystals of nitroguanidine were dried to constant weight in the dark in a vacuum desiccator. Water used for the spike recovery, preparation of standards and for the mobile phase was purified by a Milli-Q Type 1 Reagent Grade Water System (Millipore). Water for the mobile phase was degassed by first boiling, and then, after cooling, vacuum-filtering through a Whatman CF-F microfiber filter. The water remained under vacuum for at least 1 hour prior to use.

Soils

The soil for the spike recovery study was USATHAMA standard soil (blank). Several other soils from present and former Army sites were tested for interferences.

Optimum wavelength determination

The optimum wavelength setting was determined using the stopflow scan capability of the Spectra Physics variable wavelength detector. An aqueous sample of nitroguanidine was injected onto the analytical column, and when the analyte was detected, the eluent flow was stopped and the

UV spectrum in the range 210–300 nm was recorded at a scan rate of 1 nm/s.

Kinetic study

To determine the length of time required to extract nitroguanidine from soil, a kinetic study was conducted. Actual contaminated soils were not available for these experiments; therefore, four samples of USATHAMA standard soil were contaminated in the laboratory by adding 1.0 mL of 2000-µg/L aqueous NQ to 2-g subsamples of soil. NQ concentration in the soil was thus 1 µg/g. Then, to thoroughly dry the soil and to hasten any interaction between the nitroguanidine and the soil constituents, the soil samples were baked at 50°C for 30 hours and then air dried for 56 hours. An unspiked soil was treated in the same manner.

The soil samples were extracted with 50.0 mL of water in a 2.5- × 20-cm glass test tube by vortex mixing for 30 seconds and sonicating in an ultrasonic bath (Cole Palmer Model 8855-10). During sonication, 5.0-mL aliquots were removed at 5, 30, 60, 120, 240 and 480 minutes. Soil extracts were allowed to settle for 30 minutes and then filtered through Millex-HV (0.45-µm) filter units prior to analysis.

Table 3. Calibration standards for nitroguanidine.

Aliquot of 951-µg/L standard	*Capacity of volumetric flask (mL)*	*Solution concentration (µg/L)*
0.50	100	4.75
1.00	100	9.51
2.00	100	19.0
5.00	100	47.5
10.0	100	95.1
20.0	100	190
50.0	100	475

Table 4. Solutions for spike recovery test for water method.

Aliquot of 100-µg/L standard	*Capacity of volumetric flask (mL)*	*Solution concentration (µg/L)*
0.00	100	0.00
5.00	100	5.00
10.0	100	10.0
20.0	100	20.0
50.0	100	50.0
No dilution		100

Calibration standards

An aqueous nitroguanidine stock solution was prepared by dissolving 95.1 mg of recrystallized nitroguanidine in 1 L of water. Then two independent series of standards were prepared by first diluting the stock standard 5 to 500 mL with water to make duplicate 951-µg/L standards. Subsequent dilutions were made from these standards as shown in Table 3.

Spike recovery studies

Water

Reporting limits were obtained using the Hubaux and Vos (1970) method outlined in the USATHAMA *Installation Restoration Quality Assurance Program* (USATHAMA 1987) for Class 1 certification. Samples were spiked with known quantities of nitroguanidine and analyzed on each of four days. A spiking stock solution was prepared by dissolving 100 mg of recrystallized nitroguanidine in 1 L of water. Then, a series of spiked water samples corresponding to 0.5, 1, 2, 5 and 10 times a Target Reporting Limit (TRL) of 10 µg/L was prepared. The 10-TRL sample was made by placing 1.00 mL of the 100 mg/L stock solution in a 1-L volumetric flask and bringing the flask to volume with water. The concentration of the 10 TRL solution was further diluted as shown in Table 4. Prior to analysis, each water sample was filtered through a 0.45-µm Millex-HV filter unit using a 20-mL disposable BD syringe. The first 10 mL of filtrate was discarded and the remaining 10 mL retained for analysis.

Soil

A series of spiking solutions was prepared from the 100-mg/L spiking stock. The 10-TRL spike so-

Table 5. Spiking solutions for spike recovery test for soil method.

Aliquot of 10.0-mg/L standard	*Capacity of volumetric flask (mL)*	*Solution concentration (mg/L)*	*Equivalent* concentration in soil (µg/g)*
0.00	100	0.00	0.0
5.00	100	0.5	0.25
10.0	100	1.0	0.5
20.0	100	2.0	1.0
50.0	100	5.0	2.5
No dilution		10.0	5.0

*Assuming 1.00 mL of spike solution added to 2 g of soil.

lution was made by placing 50.0 mL of stock in a 500-mL volumetric flask and diluting to volume with water. The the 10-TRL spike solution (10.0 mg/L) was diluted to make a series of spike solutions as shown in Table 5.

Several 2-g subsamples of USATHAMA standard soil were weighed out to the nearest 0.1 g in 2.0- × 25-cm test tubes equipped with Teflon-lined screw caps. Each soil subsample was spiked with one of the spiking solutions listed in Table 5 and allowed to stand 1 hour uncapped. Then 50.0 mL of water was added and each sample vortex mixed for 30 seconds and sonicated for 2 hours. Samples were allowed to settle for 30 minutes prior to filtration through Millex-HV filter units.

RESULTS AND DISCUSSION

Column and eluent selection

Three analytical columns were tested during the method development. These included a reversed-phase LC-18 column (Supelco, Inc.), a cation exchange LC-SCX column (Supelco, Inc.), and a mixed mode RP18/cation column (Alltech Associates). Retention times for nitroguanidine using the various columns and eluents are shown in Table 6. The flow rate was 1.5 mL/min for each column–eluent combination tested.

Since the Mixed Mode column resulted in the longest retention time for nitroguanidine, it was chosen as the analytical column for this study. A longer retention time is desirable to avoid interferences from the early eluting compounds often found in environmental samples and to improve the ability to resolve NQ from other solutes.

Table 6. Retention times for nitroguanidine using three columns tested. Flow rate was 1.5 mL/min.

Column	*Eluent*	*Retention time (min)*
LC18	Water.	3.1
LC18	1:9 methanol–water.	2.5
LC18	1.4 methanol–water with ion-pairing reagent, pH=3.	2.4
LC18	Water with ion-pairing reagent, pH=3.	2.7
LCSCX	0.05 M KH_2PO_4.	2.8
LCSCX	1:9 methanol:KH_2PO_4.	2.7
RP18/Cation	0.05 M KH_2PO_4.	4.1
RP18/Cation	Water.	4.2

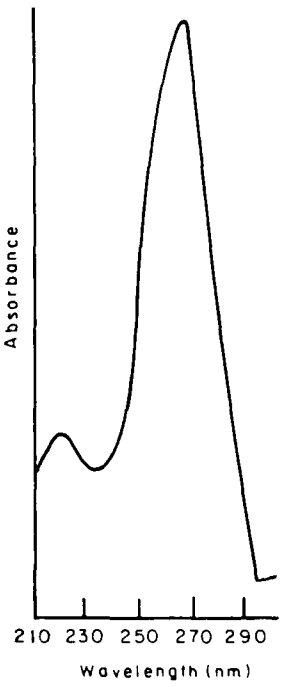

Figure 3. Optimal wavelength determination for nitroguanidine.

Optimum wavelength determination

The range 210–300 nm was scanned to determine the optimum monitoring wavelength for nitroguanidine (Fig. 3). The absorption maximum was about 263 nm.

Instrument calibration

To determine if the detector response for nitroguanidine was a linear function of analyte concentration, the calibration data were subjected to a regression analysis for a non-zero-intercept model ($y = a + bx$) and a zero-intercept model ($y = b'x$). The regression coefficients a, b and b' were estimated using the method of least squares (Table 7).

The fitted equations for both models were subjected to the Lack-Of-Fit (LOF) test (USATHAMA 1987). A linear model was found to be acceptable at the 95% confidence level. The intercept was then tested to determine if it was significantly different from zero. The F-ratio was calculated by dividing the differences between the residual sum of squares for the non-zero-intercept and zero-intercept models by the residual mean square for the model with the non-zero-intercept. Since the calculated F-ratio was less than the critical value at the 95% confidence level, the zero-intercept linear model was accepted. Thus, daily calibration may be obtained using a zero-intercept model and a single high-concentration replicated standard.

Table 7. Lack-of-fit and zero-intercept tests.

Analysis of Residual Variations

	Model with intercept Y = (611.2479980)+(199.9723840)X			*Model through the origin* Y = (200.9022340)X		
	(SS)	(df)	(MS)	(SS)	(df)	(MS)
Residual:	44,970,778.50	14	3,212,198.464	48,911,888.60	15	3,260,792.573
Total error:	34,493,653.50	8	4,311,706.687	34,493,653.50	8	4,311,706.687
Lack of fit:	10,477,125.00	6	1,746,187.500	14,418,235.10	7	2,059,747.871
	LOF *F*-ratio (*F*): 0.404987544 Critical 95% *F*: 3.58			LOF *F*-ratio (*F*): 0.477710573 Critical 95% *F*: 3.50		

Zero Intercept Hypothesis

Zero intercept accepted — Calculated *F*: 1.226919863 — Critical 95% *F*: 4.60

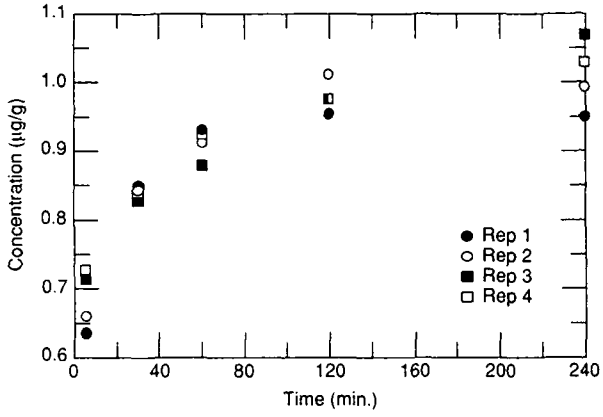

Figure 4. Kinetic study for extraction of nitroguanidine from soil.

Kinetic study

Results of a kinetic study, using water and a sonic bath to extract soil, are shown in Figure 4. Equilibrium is reached between 120 and 240 minutes. Aliquots removed at 480 minutes were a brownish-orange color, and the chromatograms for these samples contained several large peaks that prevented the baseline from returning to zero prior to the start of the NQ peak.

Extraction of various soils to test for interference

Twelve soils from various Army sites were extracted with 10.0 mL of water in a sonic bath for 480 minutes. No interfering peaks were observed in the chromatograms, but some of the extracts were extremely difficult to filter, even after centrifugation at 3500 rpm for 30 minutes. The experiment was repeated with 50.0 mL of solvent and filtration was much easier.

Spike recovery studies

Spike recovery studies were conducted to allow estimation of reporting limits. Water and soil samples were spiked over the concentration ranges of 5.0–100 µg/L and 0.25–5.0 µg/g respectively. Blank water and soil samples were also analyzed.

Certified reporting limits (CRLs) were calculated using the method of Hubaux and Vos (1970). Bartlett's test was used to compare the variances at each target level (Tables 8 and 9). For water, the range of homogeneous variance included 0.5–5 TRL levels. For soil, the range of homogeneous variance included the entire data set. The data for each of the four days were pooled and tested for lack of fit. For the water samples, data for the entire range were linear; however, the intercept was significantly different from zero. When the highest target value was dropped, the intercept's difference from zero became nonsignificant. For the data for the soil samples, the model with intercept was linear, but the model through the origin was not. The intercept (–0.089) was statistically significantly different from zero, but from a practical standpoint, this is a small difference.

CRLs were obtained from the X values corresponding to the point on the lower confidence limit curve where the Y values matched the values of Y on the upper confidence limit curve at $X = 0$ (Fig. 5). Method reporting limits were 5.0 µg/L and 0.5 µg/g for water and soil, respectively. Method accuracies, based on percent recovery, were 106 and 98%.

Table 8. Recovery of nitroguanidine during 4-day spike recovery study for water method.

Spike level	*Target concentration (µg/L)*	*Found concentration (µg/L) Day 1*	*Day 2*	*Day 3*	*Day 4*	*Mean*	*Variance*	*Bartlett's test (χ^2)*
0×	0.0	0.0	0.0	0.0	0.0			
		0.0	0.0	0.0	0.0	0.0	0.0	—
0.5×	5.0	5.11	7.22	4.96	7.66			
		5.58	6.30	6.59	9.87	6.66	2.6	—
1×	10.0	11.3	9.9	14.2	13.4			
		12.0	11.1	7.1	12.5	11.4	4.89	0.673
2×	20.0	24.0	23.0	22.7	22.3			
		22.2	22.0	22.1	25.2	22.9	1.26	2.96
5×	50.0	52.5	55.9	53.9	53.1			
		50.3	51.7	54.8	58.1	53.8	6.12	4.45
10×	100	102	104	104	95.9			
		105	111	104	93.0	102	31.3	20.4*

*Critical χ^2 value (α = 0.05, df = 4) = 9.49.

Table 9. Recovery of nitroguanidine during 4-day spike recovery study for soil method.

Spike level	*Target concentration (µg/L)*	*Found concentration (µg/L) Day 1*	*Day 2*	*Day 3*	*Day 4*	*Mean*	*Variance*	*Bartlett's test (χ^2)*
0×	0.0	0.0	0.0	0.0	0.0			
		0.0	0.0	0.0	0.0	0.0	0.0	—
0.5×	0.25	0.247	0.226	0.344	0.173			
		0.296	0.431	0.107	0.209	0.254	0.0103	—
1×	0.5	0.447	0.407	0.302	0.408			
		0.457	0.325	0.347	0.552	0.406	0.0066	0.332
2×	1.0	0.929	0.727	0.955	0.927			
		0.879	0.720	0.591	0.850	0.822	0.0167	1.43
5×	2.5	2.04	2.53	2.16	2.24			
		2.64	2.26	2.30	2.33	2.31	0.0371	5.60
10×	5.0	5.21	4.95	4.87	4.82			
		4.98	4.91	4.83	4.52	4.89	0.0370	7.20

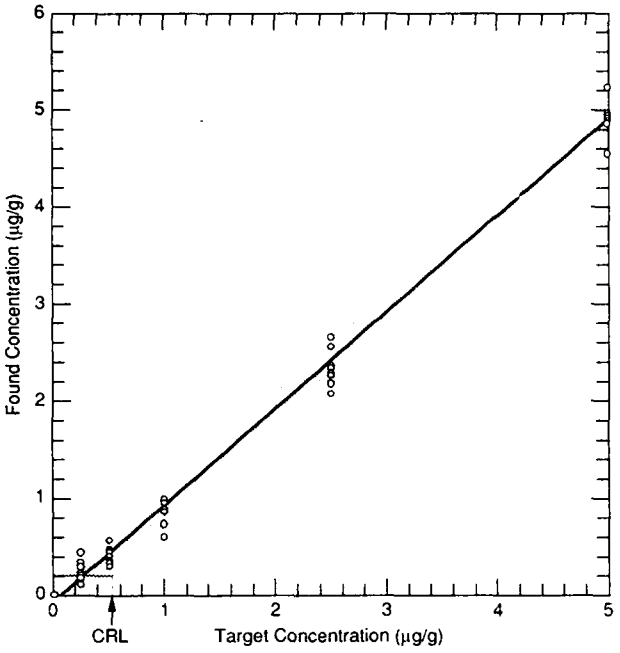

Figure 5. The reporting limit determination for nitroguanidine.

CONCLUSIONS

Methods were developed for determining nitroguanidine in soil and water. Soils are extracted with water for 2 hours in a sonic bath, then the extracts are filtered through 0.45-µm membranes. Water samples are simply filtered. Nitroguanidine is determined for both by RP-HPLC on a mixed-mode RP18/Cation column eluted with 1.5 mL/min of water and a UV detector set at 263 nm. Calibration data were found to be linear over the range 4.75–951 µg/L. Spike recovery tests were carried out. Certified reporting limits were estimated at 5.0 µg/L and 0.5 µg/g for water and soil respectively.

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APPENDIX A: COMPUTER OUTPUT FOR USATHAMA IRPQAP SOFTWARE

Part 1: CRL for water

CERTIFICATION ANALYSIS — Report Date: 10/17/88

Method Name: NQWATCERTTRUN1 — Laboratory: CR
Compound: NQ — Analysis Date: 04/18/88
Units of Measure: UGL — Matrix: WA

ANALYSIS OF RESIDUAL VARIATIONS

	--- Model with Intercept --- Y = (0.787082774) + (1.062316560)X			- Model through the Origin - Y = (1.084567500)X		
	(SS)	(df)	(MS)	(SS)	(df)	(MS)
Residual:	127.9344540	30	4.264481800	135.6672240	31	4.376362065
Total Error:	104.0753120	28	3.716975429	104.0753120	28	3.716975429
Lack of Fit:	23.85914200	2	11.92957100	31.59191200	3	10.53063733
	LOF F-Ratio(F): 3.209483417			LOF F-Ratio(F): 2.833119975		
	Critical 95% F: 3.34			Critical 95% F: 2.95		

ZERO INTERCEPT HYPOTHESIS

Zero Intercept Accepted — Calculated F: 1.813296518 Critical 95% F: 4.17

****

TABLE OF DATA POINTS — Targets: 4 — Measures per Target: 5

	Target Value	Found Concentration				
1:	5	5.1100000	5.5800000	7.2200000	6.3000000	4.360000
		6.5900000	7.6600000	9.8700000		
2:	10	12	9.9000000	11.100000	14.200000	7.100000
		13.400000	12.490000	11.300000		
3:	20	24	22.200000	23	22	22.700000
		22.100000	22.300000	25.200000		
4:	50	52.500000	50.300000	55.900000	51.700000	54.800000
		53.120000	58.110000	53.900000		

*** END OF CERTIFICATION LACK OF FIT DATA TABLE ***

CERTIFICATION ANALYSIS — Report Date: 10/17/88

Method Name: NQWATCERTTRUN1 — Laboratory: CR
Compound: NQ — Analysis Date: 04/18/88
Units of Measure: UGL — Matrix: WA

TABLE OF RESULTS FOR TRUNCATED DATA SET

Target Concentration	Standard Deviation	Percent Inaccuracy	Percent Imprecision
5	1.6129426	33.225000	24.213813
10	2.2109335	14.362500	19.332679
20	1.1236897	14.687500	4.8989197
50	2.4729360	7.5825000	4.5972830

CERTIFICATION ANALYSIS

Report Date: 10/17/88

Method Name: NQWATCERTTRUN1
Compound: NQ
Units of Measure: UGL

Laboratory: CR
Analysis Date: 04/18/88
Matrix: WA

TABLE OF DATA POINTS

Target Concentration	Found Concentration
0	0
	0
	0
	0
	0
	0
	0
	0
5	5.1100000
	5.5800000
	7.2200000
	6.3000000
	4.9600000
	6.5900000
	7.6600000
	9.8700000
10	12
	9.9000000
	11.100000
	14.200000
	7.1000000
	13.400000
	12.490000
	11.300000
20	24
	22.200000
	23
	22
	22.700000
	22.100000
	22.300000
	25.200000
50	52.500000
	50.300000
	55.900000
	51.700000
	54.800000
	53.120000
	58.110000
	53.900000

CERTIFICATION ANALYSIS

Report Date: 10/17/88

Method Name: NQWATCERTTRUN1
Compound: NQ
Units of Measure: UGL

Laboratory: CR
Analysis Date: 04/18/88
Matrix: WA

-- REGRESSION EQUATION --
Y = 1.0657816X + 0.8469620

-- UPPER REPORTING LIMIT --
50

-- SLOPE --
1.0657816

SUMMARY TRUNCATION TABLE

Target Concentrations Used	Slope	% Change from Total Data Set	% Change from Previous Data Set
Entire data set	1.0657816	0	0
minus 1 highest	1.1308000	6.1005324	6.1005324

Target Concentrations Used	Certified Reporting Limit	Upper Reporting Limit
Entire data set	5.6946876	50
Minus 1 highest	4.6198283	50

Part 2: CRL for soil

CERTIFICATION ANALYSIS — Report Date: 10/17/88

Method Name: NQSOIL — Laboratory: CR
Compound: NQ — Analysis Date: 07/29/88
Units of Measure: UGG — Matrix: SO

ANALYSIS OF RESIDUAL VARIATIONS

	--- Model with Intercept --- Y = (-0.08894155) + (0.986738673)X			- Model through the Origin - Y = (0.961473129)X		
	(SS)	(df)	(MS)	(SS)	(df)	(MS)
Residual:	0.922425334	38	0.024274351	1.072559690	39	0.027501531
Total Error:	0.754891125	35	0.021568318	0.754891125	35	0.021568318
Lack of Fit:	0.167534209	3	0.055844736	0.317668565	4	0.079417141

LOF F-Ratio(F): 2.589202213 — LOF F-Ratio(F): 3.682120311
Critical 95% F: 2.92 — Critical 95% F: 2.69
Data Not Linear

ZERO INTERCEPT HYPOTHESIS

Zero Intercept Rejected Calculated F: 6.184896834 Critical 95% F: 4.17
Model not linear through Origin

****

TABLE OF DATA POINTS — Targets: 5 — Measures per Target: 8

	Target Value	Found Concentration				
1:	0.2500000	0.2470000	0.2960000	0.2260000	0.4310000	0.3440000
		0.1070000	0.1730000	0.2090000		
2:	0.5000000	0.4470000	0.4570000	0.4070000	0.3250000	0.3020000
		0.3470000	0.4080000	0.5520000		
3:	1	0.9290000	0.8790000	0.7270000	0.7200000	0.9550000
		0.5910000	0.9270000	0.8500000		
4:	2.5000000	2.0420000	2.6390000	2.5320000	2.2600000	2.1600000
		2.3000000	2.2400000	2.3350000		
5:	5	5.2120000	4.9810000	4.9500000	4.9100000	4.8700000
		4.8300000	4.8210000	4.5230000		

*** END OF CERTIFICATION LACK OF FIT DATA TABLE ***

CERTIFICATION ANALYSIS — Report Date: 10/17/88

Method Name: NQSOIL — Laboratory: CR
Compound: NQ — Analysis Date: 07/29/88
Units of Measure: UGG — Matrix: SO

TABLE OF RESULTS FOR TRUNCATED DATA SET

Target Concentration	Standard Deviation	Percent Inaccuracy	Percent Imprecision
0.2500000	0.1015740	1.6500000	39.970075
0.5000000	0.0814686	-18.87500	20.084697
1	0.1292757	-17.77500	15.722193
2.5000000	0.1926789	-7.460000	8.3284573
5	0.1924833	-2.257500	3.9385804

CERTIFICATION ANALYSIS

Report Date: 10/11/88

Method Name: NQSOIL
Compound: NQ
Units of Measure: UGG

Laboratory: CR
Analysis Date: 07/29/88
Matrix: SO

TABLE OF DATA POINTS

Target Concentration	Found Concentration
0	0
	0
	0
	0
	0
	0
	0
	0
0.2500000	0.2470000
	0.2960000
	0.2260000
	0.4310000
	0.3440000
	0.1070000
	0.1730000
	0.2090000
0.5000000	0.4470000
	0.4570000
	0.4070000
	0.3250000
	0.3020000
	0.3470000
	0.4080000
	0.5520000
1	0.9290000
	0.8790000
	0.7270000
	0.7200000
	0.9550000
	0.5910000
	0.9270000
	0.8500000
2.5000000	2.0420000
	2.6390000
	2.5320000
	2.2600000
	2.1600000
	2.3000000
	2.2400000
	2.3350000

CERTIFICATION ANALYSIS

Report Date: 10/11/88

Method Name: NQSOIL
Compound: NQ
Units of Measure: UGG

Laboratory: CR
Analysis Date: 07/29/88
Matrix: SO

TABLE OF DATA POINTS

Target Concentration	Found Concentration
5	5.2120000
	4.9810000
	4.9500000
	4.9100000
	4.8700000
	4.8300000
	4.8210000
	4.5230000

CERTIFICATION ANALYSIS

Report Date: 10/17/88

Method Name: NQSOIL
Compound: NQ
Units of Measure: UGG

Laboratory: CR
Analysis Date: 07/29/88
Matrix: SO

-- REGRESSION EQUATION --
Y = 0.9792467X + -0.062568

-- UPPER REPORTING LIMIT --
5

-- SLOPE --
0.9792467

SUMMARY TRUNCATION TABLE

Target Concentrations Used	Slope	% Change from Total Data Set	% Change from Previous Data Set
Entire data set	0.9792467	0	0
minus 1 highest	0.9230807	5.7356363	5.7356363

Target Concentrations Used	Certified Reporting Limit	Upper Reporting Limit
Entire data set	0.5062041	5
Minus 1 highest	0.4621542	5

APPENDIX B: REVERSED-PHASE HPLC METHOD FOR THE DETERMINATION OF NITROGUANIDINE IN WATER AND SOIL IN USATHAMA FORMAT

Part 1: Water

Reversed-Phase HPLC Method for the Determination of Nitroguanidine in Water

I Summary

A. Analytes: The compound nitroguanidine can be determined using this method.

B. Matrix: The method is suitable for determination of nitroguanidine in water.

C. General Method: The method involves filtration of water samples followed by RP-HPLC determination on a mixed-mode Alltech RP18/cation column with detection using a variable wavelength UV detector set at 263 nm.

II. Application

A. Tested Concentration Range: Linearity tests were conducted using peak height measurements. For a 100-μL injection volume, this method was found to be linear over the concentration range of 4.75-950 μg/L.

B. Sensitivity: The response of the UV detector at 263 nm for nitroguanidine was estimated at 1.17×10^{-4} absorbance units at the certified reporting limit given below.

C. Reporting Limit: The reporting limit as determined over four days using the method of Hubaux and Vos (1970) was 5.0 μg/L using a 100-μL injection volume.

D. Interferences: No interferences were found.

E. Analysis Rate: Approximately 40 samples can be analyzed in a day.

F. Safety Information: Normal laboratory safety practices should be used. Nitroguanidine will not explode without a detonator.

III. Apparatus and Chemicals

A. Glassware/Hardware:

1) Filters: 0.45-μm Millex-HV, disposable.

2) Pipettes: volumetric, glass.

3) Scintillation vials: 20-mL, glass.

4) Disposable syringes: Plastipak, 10 mL or 20 mL.

5) Injection syringe: Hamilton, liquid syringe, 500 μL or autosampler vials.

6) Analytical balance: ±0.1 mg.

B. Instrumentation:

1) HPLC: Perkin Elmer Series 3, Spectra-Physics 8810 (or equivalent) and a variable wavelength UV detector such as a Perkin Elmer LC-65T or a Spectra-Physics 8490 (or equivalent).

2) Strip chart recorder.

3) Digital integrator with disk drive (HP-3393A with HP9114B or equivalent).

4) Mixed-Mode RP18/cation (Alltech Associates) HPLC column, 250 x 4.6 mm (100 Å).

5) Dynatech Model LC 241 Autosampler (or equivalent) equipped with a 100-μL loop injector.

C. Analyte:

Nitroguanidine.

Boiling point: NA.

Melting point: 232°C.

Solubility in water: at 25°C is 4.4 g/L, at 100°C is 82.5 g/L.

CAS [556-88-7].

D. Reagents:

1) Nitroguanidine: reagent grade.

2) Water: reagent grade.

IV. Calibration

A Initial Calibration:

1) Preparation of Standards: The nitroguanidine is first recrystallized from water. The recrystallized nitroguanidine is then dried to constant weight in a vacuum desiccator in the dark.

About 95 mg is transferred to a 1-L volumetric flask and the flask is brought to volume with reagent grade water. The flask is inverted several times until the nitroguanidine is dissolved. The stock solution concen-

tration is about 95 mg/L. An intermediate standard is prepared by adding 5 mL of stock to a 500-mL flask and filling the flask to volume. The concentration of the intermediate standard is 950 μg/L.

Injection standards are prepared by diluting the intermediate standard. Calibration standards containing 0, 4.75, 9.50, 19.0, 47.5, 95.0, 190, and 475 μg/L are prepared by placing 0, 0.5, 1.0, 2.0, 5.0, 10.0, 20.0, and 50.0 mL of the intermediate standard in a series of 100-mL volumetric flasks and filling to volume with water. Two independent sets of injection standards are prepared.

2) Instrument Calibration: Standards over the concentration range of interest are sequentially analyzed in random order. Peak heights are obtained. The retention time is about 4.4 min using a flow rate of 1.5 mL/min.

3) Analysis of Calibration Data: The acceptability of a linear model with zero intercept is assessed using the protocol specified in USATHAMA QA (2nd Edition, March 1987). When a linear model with zero intercept is proven to be appropriate, the slope of the best fit regression line is then equivalent to a response factor. This response factor can be compared with values obtained from replicate analyses of a single standard each day.

B. Daily Calibration:

The intermediate standard (950 μg/L) can be used for daily calibration. This standard is analyzed in triplicate at the beginning of the analysis, singly after each five samples and singly after the last sample of the day. A response factor is obtained from the mean peak height obtained over the course of the day and compared with the response factor obtained for initial calibration. These values must agree within ±10% for the first seven days following the initial calibration and on subsequent days must be within ±2 standard deviations or a new initial calibration must be obtained.

V. Certification Testing

A. Preparation of Spiked Solutions: An analyte spiking solution is prepared in a manner identical to that described for the calibration stock.

except that 100 mg of recrystallized nitroguanidine is weighed out. An intermediate spike solution is prepared by adding 1 mL of the stock tc a 1-L volumetric flask and filling the flask to volume with water. This intermediate spike solution has a concentration of 100 μg/L.

A series of spike solutions (0, 5.0, 10.0, 20.0, and 50.0 μg/L) is prepared by placing 0, 5.0, 10.0, 20.0, and 50.0 mL of the intermediate spike solution into a series of 100-mL volumetric flasks and diluting to volume with water. Duplicate spike solutions are made.

B. Analysis of Water Spikes: Water spikes are processed and analyzed as described below for real samples.

VI. Sample Handling and Storage

A. Sampling Procedure: Representative subsamples are taken for analysis.

B. Containers: All glass containers used to store water samples should be cleaned according to procedures specified in the USATHAMA QA Manual and rinsed with water.

C. Storage: All water samples should be stored at 4°C until analysis.

D. Holding Time Limits: Samples should be processed as soon as possible after receipt.

VII. Procedure

A. Filtration: A 20-mL portion of each water sample is filtered using a Plastipak syringe and a 0.45-μm Millex-HV filter unit. The first 10 mL of the filtrate is discarded, and the remainder is retained for analysis.

B. Determination: Determination of analyte concentration in the samples is obtained by RP-HPLC-UV on a variable wavelength detector set at 263 nm. By use of an autosampler, the 100-μL injection loop is flushed for 60 s with sample (0.5 mL), then the sample is injected onto a Mixed-Mode RP-18/cation column eluted with 1.5 mL/min of degassed water. The retention time for nitroguanidine is 4.4 min, and a capacity factor based on an

unretained peak for nitrate is 0.76. A chromatogram obtained for nitroguanidine is shown in Figure 1.*

VIII. Calculations

A. Response Factor: Since a linear calibration curve with zero intercept is to be expected, results will be calculated daily using a response factor. The mean response ($\bar{R}$) for nitroguanidine is obtained in peak height units. The response factor is obtained by dividing the mean response by the known solution concentration (C) in units of $\mu g/L$.

$$RF = \frac{\bar{R}}{C}$$

B. Analyte Concentrations: Solution concentrations ($\mu g/L$) in the water samples (C_a) are obtained by dividing the response obtained for each sample (R_a) by the response factor

$$C_a = \frac{R_a}{RF}$$

IX. Daily Quality Control

A. Control Spikes: Spiked water samples are prepared as described for Class 1 methods in the USATHAMA QA Manual (2nd Edition, March 1987). For each analytical lot, a method blank, a single spike at two times the certified reporting limit and duplicate spikes at ten times the certified reporting limit are analyzed. Control spikes are prepared using the appropriate spiking solution in a manner identical to that described in section V.

B. Control Charts: The control charts required are described for Class 1 methods in USATHAMA QA Manual (2nd Edition, March 1987). Standard Shewhart $\bar{X}$ and R charts for the duplicate high spikes and moving average $\bar{X}$ and R charts for the single low spike are required. Details on the charting procedures are specified in USATHAMA QA Manual (2nd Edition, March 1987).

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*Figure 1 is in the main text of this report.

X. References

Hubaux A. and G. Vos (1970) Decision and detection limits for linear calibration curves. Analytical Chemistry, 42:840-855.

USATHAMA (1987) U.S. Army Toxic and Hazardous Materials Agency Installation Restoration Quality Assurance Program. Aberdeen Proving Ground, Maryland 21010.

Part 2: Soil

Reversed-Phase HPLC Method for the Determination of Nitroguanidine in Soil

I. Summary

A. Analytes: The compound nitroguanidine can be determined using this method.

B. Matrix: The method is suitable for determination of nitroguanidine in soil.

C. General Method: The method involves extraction of air-dried soil samples with water in a sonic bath for 2 hours, filtration of soil extracts, and determination by RP-HPLC on a mixed-mode Alltech RP18/cation column with detection using a variable wavelength UV detector set at 263 nm.

II. Application

A. Tested Concentration Range: Linearity tests were conducted using peak height measurements. For a 100-μL injection volume, this method was found to be linear over the concentration range of 0.125-25.0 μg/g using the sample weight and extract volume presented later.

B. Sensitivity: The response of the UV detector at 263 nm for nitroguanidine was estimated at 1.17×10^{-4} absorbance units at the certified reporting limit given below.

C. Reporting Limit: The reporting limit as determined over four days using the method of Hubaux and Vos (1970) was 0.51 μg/g using a 100-μL injection volume.

D. Interferences: No interferences were found. Interferences from melamine and guanidine nitrate are minimized since melamine is insoluble in water and the relative absorptivity of guanidine nitrate at 263 nm is small.

E. Analysis Rate: Approximately 40 samples can be analyzed in a day.

F. Safety Information: Normal laboratory safety practices should be used. Nitroguanidine will not explode without a detonator.

III. Apparatus and Chemicals

A. Glassware/Hardware:

1) Filters: 0.45-μm Millex-HV, disposable.

2) Pipettes: volumetric, glass.

3) Test tubes: 2.5 x 20 cm, screw caps with Teflon liners.

4) Disposable syringes: Plastipak, 3 mL.

5) Injection syringe: Hamilton, liquid syringe, 500 μL or autosampler vials.

6) Analytical balance: ±0.1 mg.

B. Instrumentation:

1) HPLC: Perkin Elmer Series 3 or Spectra-Physics 8810 (or equivalent) and a variable wavelength UV detector such as a Perkin Elmer LC-65T or a Spectra-Physics 8490 (or equivalent).

2) Strip chart recorder.

3) Digital integrator with disk drive (HP-3393A with HP9114B or equivalent).

4) Mixed-Mode RP18/cation (Alltech Associates) HPLC column, 250 x 4.6 mm (100 Å).

5) Dynatech Model LC 241 Autosampler (or equivalent) equipped with a 100-μL loop injector.

6) Sonic Bath (Cole Palmer Model 8855-10 or equivalent).

7) Vortex mixer (Thermolyne Type 37600 or equivalent).

C. Analyte:

Nitroguanidine.

Boiling point: NA.

Melting point: 232°C.

Solubility in water: at 25°C is 4.4 g/L, at 100°C is 82.5 g/L.

CAS [556-88-7].

D. Reagents

1) Nitroguanidine: Reagent grade.

2) Water: Reagent grade.

IV. Calibration

A. Initial Calibration:

1) Preparation of Standards: The nitroguanidine is first recrystallized from water. The recrystallized nitroguanidine is then dried to constant weight in a vacuum desiccator in the dark.

About 100 mg is transferred to a 1-L volumetric flask and the flask is brought to volume with reagent grade water. The flask is inverted several times until the nitroguanidine is dissolved. The stock solution concentration is about 100.0 mg/L. An intermediate standard is prepared by adding 5.00 mL of stock to a 500-mL flask and filling the flask to volume. The concentration of the intermediate standard is 1000 μg/L.

Injection standards containing 0, 5.00, 10.0, 20.0, 50.0, 100, 200, and 500 μg/L are prepared by placing 0, 0.50, 1.00, 2.00, 5.00, 10.0, 20.0, and 50.0 mL of the intermediate standard in a series of 100-mL volumetric flasks and filling to volume with water. These concentrations correspond to 0, 0.12, 0.25, 0.50, 1.25, 2.50, 5.00, and 12.5 μg/g assuming 2.0 g of soil are extracted with 50.0 mL of water. Two independent sets of injection standards are prepared.

2) Instrument Calibration: Standards over the concentration range of interest are sequentially analyzed in random order. Peak heights are obtained. The retention time is about 4.2 min using a flow rate of 1.5 mL/min.

3) Analysis of Calibration Data: The acceptability of a linear model with zero intercept is assessed using the protocol specified in USATHAMA QA (2nd Edition, March 1987). A linear model with zero intercept has been found to be appropriate, and thus the slope of the best fit regression line is equivalent to a response factor. This response factor can be compared with values obtained from replicate analyses of a single standard each day.

B. Daily Calibration:

Since the zero intercept model is generally applicable, the intermediate standard (500 μg/L) can be used for daily calibration. This standard is analyzed in triplicate at the beginning of the analysis, singly after each five samples and singly after the last sample of the day. A

response factor is obtained from the mean peak height obtained over the course of the day and compared with the response factor obtained for initial calibration. These values must agree with the initial calibration within ±10% for the first seven daily calibrations, and subsequently must be within ±2 standard deviations or a new initial calibration must be obtained.

V. Certification Testing

A. Preparation of Spiking Solutions: An analyte spiking solution is prepared in a manner identical to that described for the calibration stock. An intermediate spike solution is prepared by adding 50.0 mL of the stock to a 500.0-mL volumetric flask and filling the flask to volume with water. This intermediate spike solution has a concentration of 10,000 μg/L.

A series of spike solutions (0, 500.0, 1000.0, 2000.0, and 5000.0 μg/L) is prepared by placing 0, 5.0, 10.0, 20.0, and 50.0 mL of the intermediate spike solution in a series of 100-mL volumetric flasks and diluting the volume with water. These solutions correspond to 0, 0.5, 1, 2, and 5 times the target reporting limit. The intermediate spike solution serves as the 10X spike.

B. Preparation of Control Spikes: Spiked soil samples are prepared by placing a series of 2.00-g subsamples of USATHAMA Standard Soil in individual 2.5- x 20-cm glass test tubes. Each soil sample is spiked with 1.00 mL of one of the spiking solutions described above and allowed to equilibrate for 1 hour prior to extraction.

C. Analysis of Soil Extracts: Soil extracts are processed and analyzed as described below for real samples.

VI. Sample Handling and Storage

A. Sampling Procedure: Representative subsamples are taken for analysis.

B. Containers: All glass containers used to store soil samples should be cleaned according to procedures specified in the USATHAMA QA Manual and rinsed with water.

C. Storage: All soil samples should be stored at 4°C until analyzed.

D. Soil Drying: Soil samples are air dried to constant weight and ground with a mortar and pestle prior to extraction.

E. Holding Time Limits: Samples should be processed as soon as possible after receipt.

VII. Procedure

A. Soil Extraction: A 2.00-g subsample of each air-dried soil is placed in individual 2.5- x 20-cm glass test tubes with screw caps. A 50.0-mL aliquot of reagent grade water is added to each tube. The tubes are capped, vortex mixed for 30 s, and placed in a sonic bath for 2 hours.

The samples are removed from the sonic bath and allowed to cool and settle for 30 min. A 6-mL portion of each soil extract is filtered using a Plastipak syringe and a 0.45-μm Millex-HV filter unit. The first 3 mL of the filtrate is discarded, and the remainder is retained for analysis. If necessary, the soil extracts may be centrifuged to enhance ease of filtration.

B. Determination: Determination of analyte concentration in the samples is obtained by RP-HPLC-UV on a variable wavelength detector set at 263 nm. By use of an autosampler, 100-μL injection loop is flushed for 60 s (0.5 mL) with sample, then the sample is injected onto a Mixed-Mode RP-18/cation column eluted with 1.5 mL/min of degassed water. The retention time for nitroguanidine is 4.2 min, and a capacity factor based on an unretained peak for nitrate is 0.76. A chromatogram obtained for nitroguanidine is shown in Figure 1.*

VII. Calculations

A. Response Factor: Since a linear calibration curve with zero intercept is to be expected, results will be calculated daily using a response factor. The mean response ($\bar{R}$) for nitroguanidine in the standard is

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*Figure 1 is in the main text of this report.

obtained in peak height units. The response factor is obtained by dividing the mean response by the known solution concentration (C) in units of $\mu g/L$.

$$RF = \frac{\bar{R}}{C}$$

B. Analyte Concentrations: Solution concentrations ($\mu g/L$) in the soil extracts (C_a) are obtained by dividing the response obtained for each sample (R_a) by the response factor

$$C_a = \frac{R_a}{RF}$$

Concentration in soil $\left(X_a\right)$, on a $\mu g/g$ basis, is then obtained by multiplying solution concentrations by the volume of extraction solvent (0.050 L) and dividing by the actual mass of dry soil extracted (M).

$$X_a = \frac{C_a \times (0.050)}{M}$$

IX. Daily Quality Control

A. Control Spikes: Spiked soil samples are prepared as described for Class 1 methods in the USATHAMA QA Manual (2nd Edition, March 1987). For each analytical lot, a method blank, a single spike at two times the certified reporting limit and duplicate spikes at ten times the certified reporting limit are analyzed. Control spikes are prepared using the appropriate spiking solution in a manner identical to that described in section V.

B. Control Charts: The control charts required are as described for Class 1 methods in USATHAMA QA Manual (2nd Edition, March 1987). Standard Shewhart $\bar{X}$ and R charts for the duplicate high spikes and moving average $\bar{X}$ and R charts for the single low spike are required. Details on the charting procedures are specified in USATHAMA QA Manual (2nd Edition, March 1987).

X. References

Hubaux A. and G. Vos (1970) Decision and detection limits for linear calibration curves. Analytical Chemistry, 42:840-855.

USATHAMA (1987) U.S. Army Toxic and Hazardous Materials Agency Installation Restoration Quality Assurance Program. Aberdeen Proving Ground, Maryland 21010.